surpassed as soon as the noise reduction factor is less than 0.5. This is typically quantified by the improvement of the signal-to-noise ratio. Brida *et al.* report a noise reduction factor (below the classical border) of about 0.45 (±0.005) for their imaging method when capturing the intensity pattern with a CCD camera and taking mean values over large spatial samples.

To achieve this quantum-enhanced noise reduction, several significant improvements over former experiments[5] were necessary. Correlated photon pairs were generated using a β-barium borate nonlinear crystal pumped with the third harmonic (355 nm) of a Q-switched Nd:YAG laser with a repetition rate of 10 Hz and a pulse width of 5 ns. The image of a weakly absorbing object — a π-shaped titanium deposition — was obtained by capturing the intensity pattern of the photons in the optical and reference channel with a CCD camera (Fig. 1). The noise reduction factor σ is directly dependent on the optical channel's transmittance η by the relation $\sigma = 1 - \eta$; the higher the absorption of the object (and thus the loss of photons), the smaller will be the improvement for the imaging. It is therefore experimentally challenging to balance the parameters for imaging in the quantum regime.

Furthermore, the pump beam's finite waist leads to momentum uncertainties in the created photons, which decrease the coherence area in the photon numbers. The last technical challenge is the ratio between the coherence area and the pixel dimensions. Because a quantum correlation in photon numbers can only be obtained while the detection area is larger than the coherence area, this value must be sufficiently large. The authors achieved this by properly designing the pump beam and by expanding the detection area to create 'superpixels' of combined pixels.

Although the experiment of Brida *et al.* has numerous potential applications for imaging with low photon fluxes, several limitations currently exist. First, the transmittance in the optical channel must be as high as possible to achieve a sufficient noise-reduction factor. This requires all objects and optical elements within a system to be weakly absorbing and of low photon loss. Second, preparation of the down-converted light is demanding: the inhomogeneities of the signal and idler beams must be eliminated and the spectral band must be chosen around the centre wavelength. Unfortunately, the optimization of the beams' preparation is in conflict with the best possible transmittance. Thus, all the parameters for the experiment cannot be optimized simultaneously, which limits this quantum-enhanced technique.

Furthermore, this technique has to be carried out without any background correction; the typical noise originating from diffuse light scattering or electronic background will always be present in the images and cannot be removed. However, other limitations such as the current challenge of increasing the ratio of the pixel size and the coherence area may be overcome in the near future. ❐

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CARBON NANOTUBES

Breaking Kasha's rule

The emission of visible light from a dye encapsulated within a carbon nanotube gives great hope and new opportunities for the design of nanoscale optoelectronic devices.

Kazuhiro Yanagi and Hiromichi Kataura

In optically functional molecules such as dyes, fluorescence (or phosphorescence) generally occurs from the excited state with the lowest energy. This is known as "Kasha's rule" — first formulated in 1950[1] by Michael Kasha — and is a general principle with only a few rare exceptions (for example, compounds such as azulene and cyclazine[2]). Now, according to recent research[3] it seems that the dye α-sexithiophene, when encapsulated in a single-wall carbon nanotube (SWCNT), exhibits emission that also breaks this rule. The finding is significant because it suggests that organic-dye–nanotube hybrid light emitters can operate at higher photon energies than first thought, reaching to visible wavelengths. It also shows that nanotubes can help shield and protect sensitive light-emitting materials from the environment, improving their stability and offering new regimes of operation.

The physical principle of Kasha's rule is as follows. In terms of energy levels, the upper excited states are usually more closely spaced than the energy gap between the lowest excited state (a singlet or triplet) and the ground state. As a result of this close spacing, the rates of non-radiative decay between the upper states far exceed the rates of luminescence, thus impeding the emission of light. Only in the lowest excited state does radiative decay become comparable to non-radiative decay. This rule was also thought to apply to SWCNTs encapsulating dye molecules, because SWCNTs and dyes are strongly coupled through π–π interactions. However, recent research by Maria Loi and co-workers[3] demonstrates an exception to this principle.

Single-wall carbon nanotubes are cylindrical graphite tubes with diameters of approximately 1 nm that exhibit either metallic or semiconducting properties depending on how the graphite sheet is rolled. In semiconducting SWCNTs, photoluminescence and electroluminescence from the lowest excited state is observed, adhering to Kasha's rule and indicating the potential of SWCNTs for optoelectronic device applications[4]. However, as the lowest excited states of semiconducting SWCNTs are in the infrared region, the emission of visible light from SWCNTs should not be possible.

Various organic and inorganic materials can be encapsulated in the inner hollow space of a carbon nanotube to create hybrid designs with new optical properties.

For nanotube–dye complexes in which the excited state of the encapsulated dye is in visible region, visible luminescence from the dye should not be possible if the interactions between the dye and SWCNT are strong, according to Kasha's rule. This is because when the encapsulated dye is photo-excited, the excited energy is transferred to the lower states of the surrounding SWCNTs, and therefore emission occurs from the lowest excited states of the semiconducting SWCNTs in the infrared (Fig. 1). Such excited energy-decay processes have been observed in SWCNTs encapsulating, for example, carotenoids and squarylium dyes[5,6]. Visible-wavelength light emission was therefore thought to be very difficult to achieve in a nanotube–dye system.

The recent work of Loi *et al.* demonstrates visible light emission from SWCNTs that contain α-sexithiophene molecules[3] — a conjugated oligomer with strong optical absorption and luminescence in the visible region. The researchers encapsulated the molecules inside the SWCNTs through a sublimation method, and observed luminescence of 550 nm from the dye molecules by photo-exciting the complexes at 380 nm. The excited state energies of the surrounding SWCNTs are below those of the dye; thus, the observed emission originated from the higher excited state of this complex, which violates Kasha's rule (Fig. 1).

It is worth noting that such violation phenomena have already been reported for double-wall carbon nanotube (DWCNT) complexes, for example in the photo-emission from inner carbon nanotubes of DWCNTs[7,8], which have inner and outer tubes in a co-axial arrangement. The lowest excited states of the semiconducting class of inner tubes are higher than those of the outer tubes because the inner tube diameters are smaller than those of the outer. Photo-emission from inner tubes in DWCNTs therefore violates Kasha's rule if the interactions between the inner and outer tubes are strong, but such emission is observed in DWCNTs produced by chemical vapour deposition processes.

The mechanism behind the violation of Kasha's rule for carbon nanotube complexes is still under discussion. Interactions between the nanotubes and the inner materials should be weak. For example, in DWCNTs produced by the decomposition of C_{60} molecules encapsulated in SWCNTs, in which interactions between the inner and the outer nanotubes are strong, emission from the inner tube is not observed[9]. It is assumed that the distance between the inner and the outer tubes is large, allowing observation of the luminescence from the inner tube. However, much more detailed studies are required to understand the origins and mechanisms of violation of Kasha's rule in nanotube complexes.

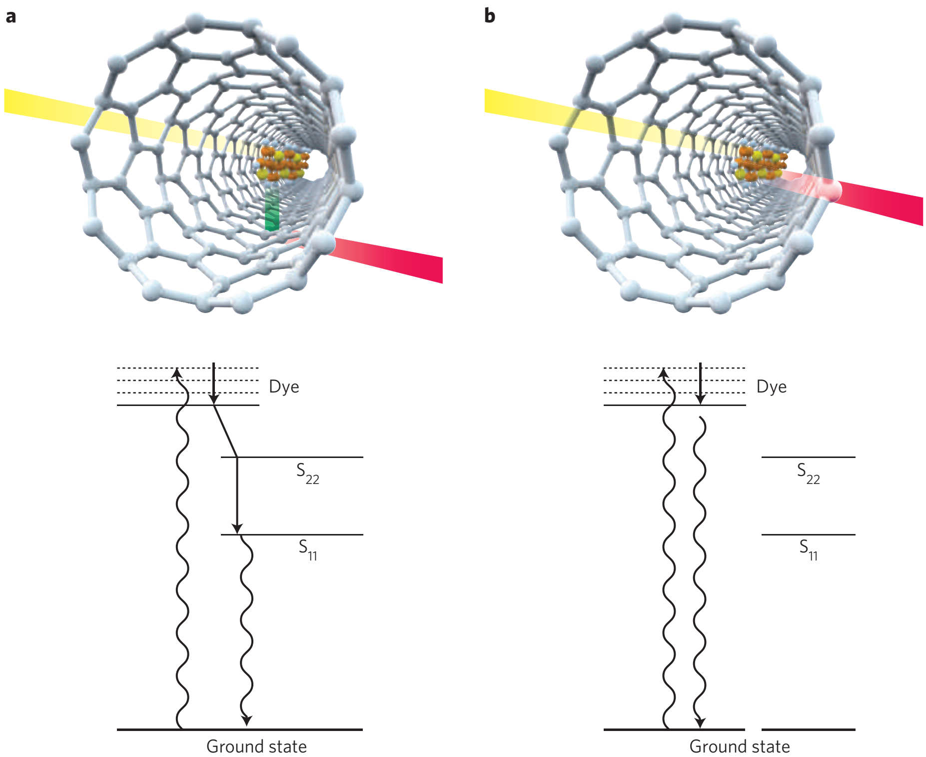

Figure 1 | Schematic of excited energy decay processes. Energies of the excited states of encapsulated dyes and the first (S_{11}) and the second (S_{22}) excited states of surrounding semiconducting SWCNTs are indicated. **a**, Decay process following Kasha's rule (strong coupling between the dye and SWCNT). When the encapsulated dye (or complex) is photo-excited, the energy decays to the lowest excited state of the complex (S_{11}) through non-radiative processes (solid lines). Emission from the S_{11} state of the surrounding SWCNTs then occurs (wavy line). **b**, Decay process that violates Kasha's rule (weak coupling between the dye and SWCNT), reported by Loi *et al.*[3]. Emission from an encapsulated dye occurs before the energy is transferred to the lowest excited state of the complex.

Although the mechanisms are not yet clarified, this violation has a great impact on the design of materials for optoelectronic devices. A huge number of optically functional nanotube compounds have been synthesized, but only a few are used for industrial applications — most have limited stability. However, in nanotube complexes (including DWCNTs), the outer nanotube walls protect the inner materials from the surrounding environment, making the inner materials particularly stable and resulting in a greatly reduced level of chemical reactivity and physical degradation. Nanotube encapsulation therefore offers a means of exploiting compounds with desirable optical functionality but low stability. If encapsulated compounds are strongly coupled to SWCNTs, luminescence from the compounds is impossible, adhering to Kasha's rule. However, in situations violating Kasha's rule through weak interactions with SWCNTs, visible light luminescence seems possible. ❐

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